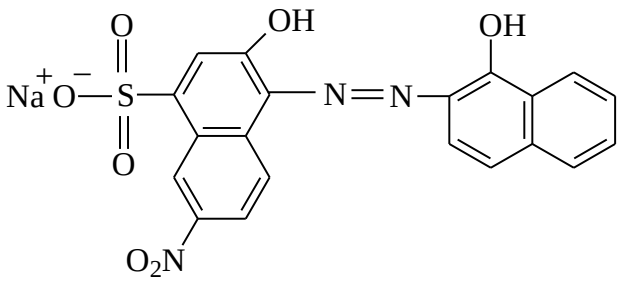
EXPERIMENT: **To determine calcium Ca^{2+} and magnesium Mg^{2+} hardness separately in the given water sample by EDTA titration method. You are provided 1 ml of EDTA= 1 mg of $CaCO_3$.**

Chemical Requirements: Hard water sample, EDTA solution, buffer solution of NH_4OH + NH_4Cl having pH 10 ± 0.1, calcium precipitating buffer solution of $(NH_4)_2C_2O_4$ + NH_4OH + NH_4Cl.

Indicator: Erichrome Black-T Indicator (Erio-T or EBT)



Sodium salt of Erichrome Black-T (represented as NaH_2In)

End point: Color change from wine red to pure blue.

Hardness: Originally, water hardness was defined as the measure of the capacity of the water to precipitate soap. It arises due to presence of dissolved salts of Ca^{2+}, Mg^{2+}, Fe^{3+} and some other heavy metal ions in water.

Calcium hardness means all the hardness due to soluble calcium salts whereas the hardness due to soluble magnesium salts is termed as magnesium hardness. It may be temporary or permanent.

EDTA method of hardness determination: It is a complexometric titration method. The principle involves the formation of 1:1 complexes of hadness causing metal ions of water with EDTA.

Theory: The total hardness (calcium and magnesium hardness) is determined by titrating a known volume of water sample, buffered to a pH ~10 with NH_4OH + NH_4Cl buffer, with a standard solution of EDTA in presence of Erichrome Black-T indicator (an azo dye).

Erio-T indicator is an organic azo dye having two phenolic ionizable hydrogen atoms. It has three different forms depending on pH:

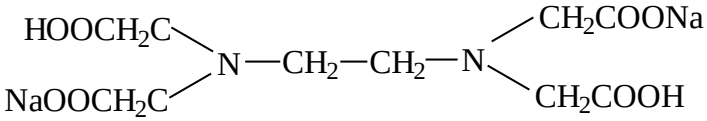
$$\underset{\text{Red}}{H_2In^-} \xrightleftharpoons{pH > 6.3} \underset{\text{Blue}}{HIn^{2-}} \xrightleftharpoons{pH > 11.5} \underset{\text{Yellowish orange}}{In^{3-}}$$

When added to hard water at a pH ~10 (maintained with ammonical buffer), it forms unstable wine red coloured complexes with bivalent metal ions of water.

$$M^{+2} + HIn^{2-} \xrightarrow{pH\sim10} MIn^{-} + H^{+}$$

(From water) ($M^{+2} = Ca^{+2}, Mg^{+2}$) (Indicator) (Metal-EBT complexes) (Wine red)

EDTA is taken in the form of its disodium salt due to higher solubility in water. It ionizes in aqueous solution to give astrong chelating ion.



Disodium salt of EDTA (Na_2H_2Y)

$$Na_2H_2Y \rightarrow 2\,Na^{+} + H_2Y^{2-}$$

Chelating ion

When added from burette to wine red solution, EDTA combines with free metal ions of hard water to form their respective soluble complexes. These are more stable than corresponding metal indicator complexes.

$$M^{+2} + H_2Y^{2-} \rightarrow MY^{2-} + 2\,H^{+}$$

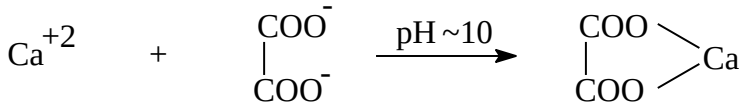
From water EDTA Metal-EDTA complexes

When all free metal ions of hard water have complexed with EDTA, a slight excess of EDTA removes metal ions from weak metal indicator complexes to form strong metal-EDTA complexes. This releases the indicator in free form which is blue in colour. This makes the end point of titration i.e. color change from wine red to pure blue.

$$MIn^{-} + H_2Y^{2-} \rightarrow MY^{2-} + HIn^{2-} + 2\,H^{+}$$

Metal-EBT complexes (Less stable) Excess Metal-EDTA complexes (More stable) Free indicator (blue)

After finding the total hardness of water sample, Ca^{2+} ions in hard water can be precipitated as calcium oxalate by adding calcium precipitating buffer solution of $(NH_4)_2C_2O_4 + NH_4OH + NH_4Cl$.



(From hard water) (Oxalate ion) (Calcium oxalate) (White ppt)

The solution is filtered to remove white ppt. i.e. calcium hardness. Titration of filtrate against standard EDTA solution using EBT indicator gives magnesium hardness in water sample. From the difference of total and magnesium hardness, calcium hardness in sample is obtained.

	Mg^{+2}	+	HIn^{2-}	→	$MgIn^{-}$ +	H^{+}
From hard water			Indicator		Mg-Indicator complex	
	Mg^{+2}	+	H_2Y^{2-}	→	MgY^{2-} +	$2\ H^{+}$
From hard water			EDTA		Mg-EDTA complex	

$MgIn^{-}$	+	H_2Y^{2-}	→	MgY^{2-}	+	HIn^{2-}	$+ 2\ H^{+}$
Mg-EBT complex		Excess		Mg-EDTA complex			Free indicator
(Less stable)				**(More stable)**			**(pure blue)**

Procedure:

Step 1. Standardization of EDTA solution

Rinse and fill the burette with standard EDTA solution and note down its initial reading. Transfer 10 ml of given standard hard water (S.H.W.) sample in a conical flask. Add $1/3^{rd}$ test tube (i.e. 5 ml) of buffer solution and 3-4 drops of Erichrome Black-T indicator. Solution becomes wine red in colour. Titrate this solution against EDTA solution till wine red colour changes to pure blue. Note down the final burette reading.

Repeat to get concordant readings. Let V_1 ml of EDTA used in this step.

Step 2. Determination of total hardness in sample

Transfer 10 ml of given hard water sample in a conical flask. Add $1/3^{rd}$ test tube (i.e. 5 ml) of buffer solution and 3-4 drops of Erichrome Black-T indicator. Solution becomes wine red in colour. Titrate this solution against EDTA solution till wine red colour changes to pure blue. Note down the final burette reading.

Repeat to get concordant readings. Let V_2 ml of EDTA used in this step.

Step 3. Ca^{2+} ions precipitation and determination of Mg^{2+} hardness in sample

Pipette out 100 ml of water sample in a 250 ml beaker. Add 25 ml of calcium precipitating buffer solution with constant stirring by glass rod. Allow the white ppt. to settle down for 20-30 minutes. Filter the solution through a dry Whatman-42 filter paper in a dry flask. Transfer 12 ml of this filtrate in a conical flask. Add $1/3^{rd}$ test tube (i.e. 5 ml) of buffer solution and 3-4 drops of Erichrome Black-T indicator. Solution becomes wine red in colour. Titrate this solution against EDTA solution till wine red colour changes to pure blue. Note down the volume of EDTA used.

Repeat to get concordant readings. Let V_3 ml of EDTA used in this step.

Observations:

Table 1: Standardization of EDTA solution

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_1 ml

Table 2: Total hardness of water sample

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_2 ml

Table 2: Mg^{2+} hardness of water sample

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_3 ml

General calculations:

Step 1. Standardization of EDTA solution

Volume of standard hard water (S.H.W.) taken for titration = 10 ml

10 ml of S.H.W. = V_1 ml of EDTA

1 ml of S.H.W. = $\frac{V_1}{10}$ mg of $CaCO_3$ (Given: 1 ml of S.H.W. = 1 mg of $CaCO_3$)

Step 2. Estimation of total hardness in sample

Volume of water sample taken for titration = 10 ml

10 ml of water = V_2 ml of EDTA

= V_2 mg of $CaCO_3$

1000 ml of water = $V_2/10 \times 1000$ mg of $CaCO_3$

Total hardness = 100 V_2 ppm in terms of $CaCO_3$

Step 3. Estimation of Mg^{2+} hardness in sample

Volume of solution prepared = 100 + 25 = 125 ml

Hardness of 125 ml of prepared solution = Mg^{2+} hardness of 100 ml hard water sample

10 ml filtrate = 100/125 × 10 = 8 ml of hard water

Concordant volume of EDTA solution used = V_3 ml

8 ml of hard water = V_3 ml of EDTA

= V_3 mg of $CaCO_3$

1000 ml hard water = $V_3/8 \times 1000$ mg of $CaCO_3$

Therefore, Mg^{2+} hardness of water sample = 100 V_3 ppm in terms of $CaCO_3$

Ca^{2+} hardness in water sample = Total hardness- Mg^{2+} hardness

= 100 V_2 – 100 V_3 ppm = X ppm in terms of $CaCO_3$

Results: The given water sample contains,

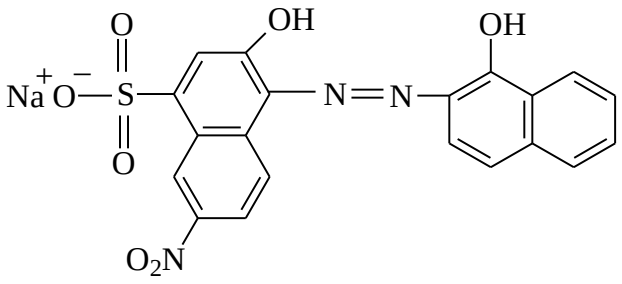
Ca^{2+} hardness in water sample = X ppm

Mg^{2+} hardness in water sample = 100 V_3 ppm

EXPERIMENT: **To determine calcium Ca^{2+} and magnesium Mg^{2+} hardness separately in the given water sample by EDTA titration method. You are provided 1 ml of EDTA= 1 mg of $CaCO_3$.**

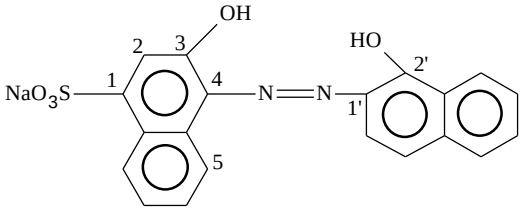
Chemical Requirements: Hard water sample, EDTA solution, buffer solution of NH_4OH + NH_4Cl having pH 10 ± 0.1, diethyl amine.

Indicator: (i) Erichrome Black-T Indicator (Erio-T or EBT)



Sodium salt of Erichrome Black-T (represented as NaH_2In)

(ii) Calcon or Solochrome dark blue



IUPAC NAME: [Sodium 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate]

End point: (i) Color change from wine red to pure blue (with EBT)

(ii) Color change from pink to purple (with Calcon)

Hardness: Originally, water hardness was defined as the measure of the capacity of the water to precipitate soap. It arises due to presence of dissolved salts of Ca^{2+}, Mg^{2+}, Fe^{3+} and some other heavy metal ions in water.

Calcium hardness means all the hardness due to soluble calcium salts whereas the hardness due to soluble magnesium salts is termed as magnesium hardness. It may be temporary or permanent.

EDTA method of hardness determination: It is a complexometric titration method. The principle involves the formation of 1:1 complexes of hardness causing metal ions of water with EDTA.

Theory: The total hardness (calcium and magnesium hardness) is determined by titrating a known volume of water sample, buffered to a pH ~10 with $NH_4OH + NH_4Cl$ buffer, with a standard solution of EDTA in presence of Erichrome Black-T indicator (an azo dye).

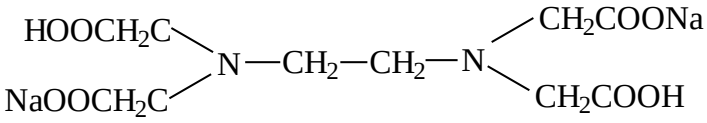
Erio-T indicator is an organic azo dye having two phenolic ionizable hydrogen atoms. It has three different forms depending on pH:

$$\underset{\text{Red}}{H_2In^-} \xrightleftharpoons{pH > 6.3} \underset{\text{Blue}}{HIn^{2-}} \xrightleftharpoons{pH > 11.5} \underset{\text{Yellowish orange}}{In^{3-}}$$

When added to hard water at a pH ~10 (maintained with ammonical buffer), it forms unstable wine red coloured complexes with bivalent metal ions of water.

$$\underset{\substack{\text{(From water)}\\ (M^{+2} = Ca^{+2}, Mg^{+2})}}{M^{+2}} + \underset{\text{(Indicator)}}{HIn^{2-}} \xrightarrow{pH\sim10} \underset{\substack{\text{(Metal-EBT complexes)}\\ \text{(Wine red)}}}{MIn^-} + H^+$$

EDTA is taken in the form of its disodium salt due to higher solubility in water. It ionizes in aqueous solution to give astrong chelating ion.



Disodium salt of EDTA (Na_2H_2Y)

$$Na_2H_2Y \rightarrow 2\,Na^+ + \underset{\text{Chelating ion}}{H_2Y^{2-}}$$

When added from burette to wine red solution, EDTA combines with free metal ions of hard water to form their respective soluble complexes. These are more stable than corresponding metal indicator complexes.

$$\underset{\text{From water}}{M^{+2}} + \underset{\text{EDTA}}{H_2Y^{2-}} \rightarrow \underset{\text{Metal-EDTA complexes}}{MY^{2-}} + 2\,H^+$$

When all free metal ions of hard water have complexed with EDTA, a slight excess of EDTA removes metal ions from weak metal indicator complexes to form strong metal-EDTA complexes. This releases the indicator in free form which is blue in colour. This makes the end point of titration i.e. color change from wine red to pure blue.

$$MIn^- + H_2Y^{2-} \rightarrow MY^{2-} + HIn^{2-} + 2\,H^+$$

Metal-EBT complexes	Excess	Metal-EDTA complexes	Free indicator
(Less stable)		(More stable)	(Blue)

After finding the total hardness of water sample, Mg^{2+} ions in hard water can be suppressed as magnesium hydroxide by adding diethyl amine which makes the pH of solution around 12.5.

$$\underset{\text{(From hard water)}}{Mg^{2+}} + 2OH^{\ominus} \xrightarrow{pH\ 12.5} Mg(OH)_2 \downarrow$$

Titration of solution against standard EDTA solution using Calcon indicator gives calcium (Ca^{2+}) hardness in water sample.

Ca^{+2}	+	Calcon	→	Ca-Calcon complex	+	H^+
From hard water		Indicator		Light pink		

Ca-Calcon complex	+	H_2Y^{2-}	→	CaY^{2-}	+	Calcon	+	2 H^+
Light pink		Excess		Ca-EDTA complex		Free indicator		
(Less stable)				**(More stable)**		**(Purple)**		

From the difference of total and calcium hardness, magnesium hardness in sample is obtained.

Procedure:

Step 1. Standardization of EDTA solution

Rinse and fill the burette with standard EDTA solution and note down its initial reading. Transfer 10 ml of given standard hard water (S.H.W.) sample in a conical flask. Add 1/3rd test tube (i.e. 5 ml) of buffer solution and 3-4 drops of Erichrome Black-T indicator. Solution becomes wine red in colour. Titrate this solution against EDTA solution till wine red colour changes to pure blue. Note down the final burette reading.

Repeat to get concordant readings. Let V_1 ml of EDTA used in this step.

Step 2. Determination of total hardness in sample

Transfer 10 ml of given hard water sample in a conical flask. Add 1/3rd test tube (i.e. 5 ml) of buffer solution and 3-4 drops of Erichrome Black-T indicator. Solution becomes wine red in colour. Titrate this solution against EDTA solution till wine red colour changes to pure blue. Note down the final burette reading.

Repeat to get concordant readings. Let V_2 ml of EDTA used in this step.

Step 3. Mg^{2+} ions suppression and determination of Ca^{2+} hardness in sample

Pipette out 10 ml of water sample in a conical flask. Add 3-4 ml of diethyl amine and 4-5 drops of Calcon indicator. Solution becomes light pink in colour. Shake the solution thoroughly for 2 minutes. Titrate this pink solution against EDTA solution till colour changes to purple. Note

down the volume of EDTA used. Repeat to get concordant readings. Let V_3 ml of EDTA used in this step.

Observations:

Table 1: Standardization of EDTA solution

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_1 ml

Table 2: Total hardness of water sample

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_2 ml

Table 3: Ca^{2+} hardness of water sample

S. No.	Initial Burette Reading	Final Burette Reading	Volume of EDTA used (ml)
1.			
2.			
3.			

Concordant volume = V_3 ml

General calculations:

Step 2. Estimation of total hardness in sample

Volume of water sample taken for titration = 10 ml

10 ml of water = V_2 ml of EDTA

= V_2 mg of $CaCO_3$

1000 ml of water = $V_2/10 \times 1000$ mg of $CaCO_3$

Total hardness = 100 V_2 ppm in terms of $CaCO_3$

Step 3. Estimation of Ca^{2+} hardness in sample

Volume of water sample taken for titration = 10 ml

10 ml of diethyl amine treated hard water = V_3 ml of EDTA

= V_3 mg of $CaCO_3$

1000 ml hard water = $V_3/10 \times 1000$ mg of $CaCO_3$

Therefore, Ca^{2+} hardness of water sample = 100 V_3 ppm in terms of $CaCO_3$

Mg^{2+} hardness in water sample = Total hardness- Ca^{2+} hardness

= 100 V_1 – 100 V_3 ppm = X ppm in terms of $CaCO_3$

Results: The given water sample contains,

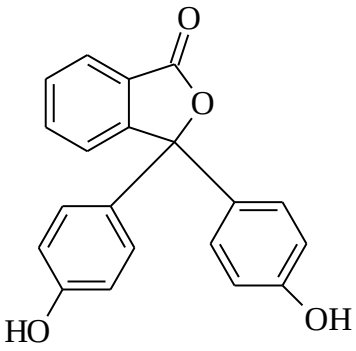
Mg^{2+} hardness in water sample = X ppm

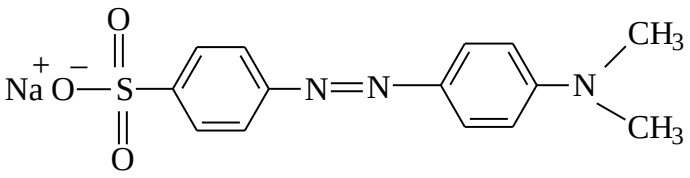
Ca^{2+} hardness in water sample = 100 V_3 ppm

EXPERIMENT: **To determine the alkalinity of given water sample. You are provided N/50 H_2SO_4.**

Chemical Requirements: Standard H_2SO_4 (N/50) solution.

Indicator: (i) Phenolphthalein (ii) Methyl orange





End Point: (i) Disappearance of pink colour with Phenolphthalein.

(ii) Colour change from light yellow to reddish orange with Methyl orange.

Alkalinity: Alkalinity of water means the total amount of those substances in water which cause an increase in OH^- ion concentration due to dissociation in water or due to hydrolysis.

Types: Alkalinity is mainly due to the presence of hydroxide ions (OH^-), carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO_3^-) present in the given sample of water. These ions may be present alone or in combination e.g.

(i) OH^- (ii) CO_3^{2-} only (iii) HCO_3^- only

(iv) $OH^- + CO_3^{2-}$ (v) $CO_3^{2-} + HCO_3^-$

The possibility of OH^- & HCO_3^- existing together is ruled out since

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$$

Theory: The type and amount of alkalinity can be estimated by titrating a known volume of water against standard acid using phenolphthalein and methyl orange as indicator in same order. The phenolphthalein end point (P) marks the neutralization of OH^- and half neutralization of CO_3^{2-} to HCO_3^- ions. The sample is further titrated with standard acid in presence of methyl orange as indicator which neutralizes all HCO_3^- ions whether present originally or obtained from CO_3^{2-}. The titration of water upto methyl orange end point (M) gives total alkalinity of water. The reactions involved are:

(i) $OH^- + H^+ \rightarrow H_2O$ } P

(ii) $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ } P

(iii) $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ } M

Phenolphthalein alkalinity (P) = $OH^- + 1/2CO_3^{2-}$

Methyl orange or total alkalinity (M) = $OH^- + CO_3^{2-} + HCO_3^-$

From the calculated values of P and M, following alkalinity corrections can be made:

S. No.	Case	Alkalinity (in ppm)		
		OH^-	**CO_3^{2-}**	**HCO_3^-**
1.	P = 0	0	0	M
2.	P = M	P or M	0	0
3.	P = 1/2M	0	2P or M	0
4.	P > 1/2M	2P-M	2(M-P)	0
5.	P < 1/2M	0	2P	M-2P

Procedure:

Rinse and fill the burette with standard acid and note down its initial reading. Pipette out 20 ml of water sample in a conical flask. Add 2 drops of phenolphthalein indicator. Solution becomes pink in colour. Titrate this solution against acid till the colour disappears. Note down the final burette reading. To the colourless solution so obtained, add 2-3 drops of methyl orange indicator. The colour of solution becomes light yellow. Titrate it further against acid till the colour changes to reddish orange. Note down the final burette reading again. Repeat to get concordant readings.

Observations:

S. No.	**IBR**	**FBR with phenolphthalein**	**FBR with methyl orange**	**Volume of acid used (ml)**	
				Upto phenolphthalein end point	**Upto Methyl orange end point**
	(x)	**(y)**	**(z)**	**A = y-x**	**B = z-x**
1.					
2.					
3.					

Concordant volume of acid used upto phenolphthalein end point A = (y-x) ml

Concordant volume of acid used upto methyl orange end point B = (z-x) ml

General calculations:

For finding phenolphthalein alkalinity (P)

Concordant volume of acid used =A ml

Applying Normality Equation

N_1V_1 = N_2V_2

(water) (Acid)

$N_1 \times 20$ = $N/50 \times A$

$N_1 = A/1000$ N

Strength in terms of $CaCO_3$ = Normality × Equivalent wt. of $CaCO_3$

= A/1000 × 50 g/L

So phenolphthalein alkalinity (P) = A/1000 × 50 × 1000 mg/L

= 50 × A ppm

For finding methyl orange alkalinity (M)

Concordant volume of acid used =B ml

Applying Normality Equation

N_1V_1 = N_2V_2

(water) (Acid)

$N_1 \times 20$ = $N/50 \times B$

$N_1 = B/1000$ N

Strength in terms of $CaCO_3$ = Normality × Equivalent wt. of $CaCO_3$

= B/1000 × 50 g/L

So methyl orange or total alkalinity (M) = B/1000 × 50 × 1000 mg/L

= 50 × B ppm

Types of alkalinity:

Since P is related to M as……, the water sample contains the following alkalinity:

(i)……. Alkalinity = ……ppm

(ii) ……. Alkalinity = ……ppm

Result: Phenolphthalein alkalinity (P) =……..ppm

methyl orange alkalinity (M) =…….ppm

Alkalinity due to……...= …….ppm

EXPERIMENT: **To determine the amount of dissolved oxygen (D.O.) in the given water sample by using Winkler's (or Iodometric) method. You are provided N/40 Hypo solution.**

Chemical Requirements: 48% Manganous sulphate solution ($MnSO_4$), 10% alkaline potassium iodide solution (KI + KOH), Conc. H_2SO_4, N/40 Hypo solution (sodium thiosulphate, $Na_2S_2O_3$).

Indicator: Freshly prepared starch solution added near the end point.

End Point: Disappearance of blue colour (Hypo in burette).

Theory: Dissolved oxygen (D.O.) is the amount of dissolved oxygen in mg present per litre of water. It depends upon the following:

1. Higher the temp. of water, lesser is its D.O..The solubility of oxygen in fresh water varies from 14.5 ppm at 0°C to about 7.5 ppm at 30°C under one atmospheric pressure.
2. Higher the atmospheric pressure, more is its D.O.
3. Higher the conc. of salts in water, lesser is its D.O.

The amount of D.O. in water can be determined by Winkler's iodometric method. In this method D.O. of water oxidizes Mn^{2+} to Mn^{4+} (manganic oxide) in alkaline medium. It is called D.O. fixation.

$$2Mn^{2+} + O_2 + 4OH^- \longrightarrow 2Mn^{4+}O(OH)_2$$

(Basis Manganic oxide)
or Hydrated Mangenese oxide

Then Mn^{4+} (manganic oxide) on acidification releases nascent oxygen which oxidizes iodide ions I^- to iodine (I_2) in acidic medium.

$$Mn^{4+}O(OH)_2 + H^+ + 2I^- \longrightarrow I_2 + Mn^{2+} + 3H_2O$$

The liberated iodine is titrated against std. hypo solution using starch as an indicator.

$$I_2 + 2e^- \longrightarrow 2I^-$$
$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The amount of hypo solution used in the titration is equivalent to the D.O. present in given water sample.

Chemical Equations:

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \downarrow$$

Basic manganic oxide (brown ppt.)

$$MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + [O]$$

$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + 2Na_2S_4O_6$

Sod. thiosulphate — Sod. tetrathionate

Starch + I_2 → Blue coloured complex

Procedure:

Fill the D.O. bottle upto brim with given water avoiding air bubbles. Fit the stopper on the mouth of bottle and to this add 1 ml 48% manganous sulphate solution ($MnSO_4$) and 1 ml of alkaline potassium iodide solution by taking precaution that tip of the burette should be inside water. Now fit the stopper on the mouth of bottle and shake it well for approx. 2-3 min. This is called D.O. fixation. Now place the bottle undisturbed for 5-10 min. till brown colour ppt. settle down. Add 2 ml of conc. H_2SO_4 by taking the same precaution that tip of the burette should be inside water. Fit the stopper again and shake it very well till brown colour ppt. dissolve. Transfer 100 ml of this brown solution to a conical flask. Rinse and fill the burette with N/40 Hypo solution and note down the initial burette reading. Now titrate with hypo till brown colour changes to pale yellow. Add 2 ml starch indicator so that colour becomes blue. Now further titrate with hypo till blue colour disappears which is end point and which is equal to the amount of D.O. (in ppm) in given water sample. Repeat the only titration procedure to get concordant readings.

Observations:

Volume of solution taken for each titration= 100 ml

S. No.	Initial Burette Reading	Final Burette Reading	Volume of hypo solution used (ml)
1.			
2.			
3.			

Concordant volume = V ml

General calculations:

Volume of hypo solution used in titration=V ml

Normality of hypo solution = N/40

Applying Normality Equation

$N_1V_1 = N_2V_2$

(water sample) (Hypo)

$N_1 \times 100 = N/40 \times V$

$N_1 = V/4000$ N

Amount of D.O. present in given water sample = Normality × Equivalent wt. of oxygen

$= V/4000 \times 8$ g/L

$= V/4000 \times 8 \times 1000$ mg/L

= V ppm

Result: The amount of D.O. present in given water sample = V ppm

AIM: To Determine the flash point and fire point of an oil by Pensky-Marten flash point apparatus.

APPARATUS/CHEMICALS REQUIRED: Pensky-Marten's flash point apparatus, Match Box, Thermometer and Lubricating oil sample.

THEORY: Flash point is the lowest temperature at which the lubricating oil gives off enough vapours that ignite for a moment when tiny flame is brought near it. Fire point is the lowest temperature at which the vapours of the oil burn continuously for at least five seconds when a tiny flame is brought near it. Generally the fire point of oil is 5 to 40°C higher than its flash point. A good lubricant should always have flash point at least above the working temperature. This ensures safety against fire hazard during storage, transport and use of lubricating oil.

Flash and fire points are used to indicate

• Fire hazard of petroleum products and evaporation loses under high temperature loses.

• It gives us the idea about the maximum temperature below which the oil can be used.

• It is used as the means of identification of specific lubricating oil.

• For detection of contamination in the given lubricating oil.

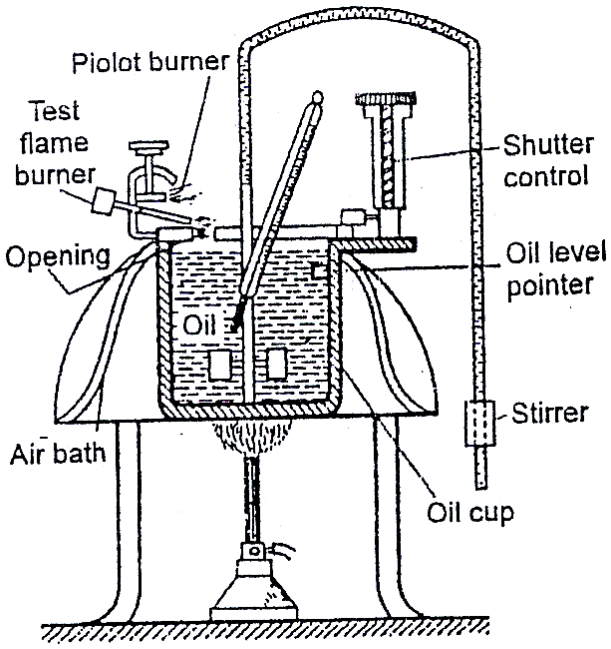


Fig. 6.1. Pensky–Marten's flash point apparatus

Flash and fire point of lubricating oils, fuel oils, solvents, solvent containing material and suspension of solids are determined by using Pensky-Marten's apparatus. It consists of three parts. An ***oil cup*** (Material- Brass; Height – 5.5cm; Diameter-5cm) is surrounded by air bath. Lid of the cup is provided with four openings of standard sizes, first opening is for stirrer, second is for admission of air, third is for thermometer and fourth is for introducing test flame. The ***shutter*** is provided at the top of the cup. By moving the shutter, opening in the lid opens and flame is dipped into this opening, bringing the flame over the oil surface. As the test flame is introduced in the opening, it get extinguished, but when the test flame is returned to its original position, it is automatically lightened by the pilot burner. ***Stove*** consists of air bath and top plate on which the flange of the cup rest. The assembly has an electric heater which heats it in a controlled manner.

PROCEDURE: Clean and dry all parts of the apparatus with the help of suitable solvent e.g. CCl4, ether, petroleum spirit or benzene and dry it to remove any traces of solvent. Fill the oil cup with the test oil up to the mark. Fix the lids on the top through which are inserted a thermometer and a stirrer. Ensure that the flame exposure device is fixed on the top. The test flame is lighted and the oil is heated at the rate of 5°C/per minute. Keep stirring the oil in the oil cup. When the temperature rises up to 15°C of the probable flash point, the test flame is introduced into the oil vapours by moving the shutter and observe for any flash (a combination of weak sound and light). Repeat this process at every one degree rise of temperature. When test flame produces a distinct flash in the oil cup, the temperature is noted down as flash point (say t_1°C). The oil sample is further heated at a rate of about 1°C/per minute and application of test

flame is done after every 1°C rise in temperature of the oil .The temperature at which oil ignites and continues to burn for 5 seconds is noted down as fire point (say t_2°C).

RESULT:

The flash point of the given oil sample = t_1 °C

The fire point of the given oil sample = t_2°C

EXPERIMENT: **Determination of viscosity of lubricant by Red Wood viscometer (No. 1 and No. 2).**

Requirements:

Redwood viscometer (No. 1 and No. 2), Stop watch, Thermometer, Given lubricating oil and distilled water.

Theory:

Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of a lubricating oil; the lowest the viscosity, greater the flow ability. It is mainly due to the forces of cohesion between the molecules of lubricating oil. **Absolute Viscosity** may be defined as "the tangential force per unit area which is required to maintain a unit velocity gradient between two parallel layers. It is denoted by η(eta). Its Unit in CGS system is poise.Mathematically,

$$\acute{\eta} = \frac{F}{A.dv/dx}$$

where F = Force, A = area, dv/dx = velocity gradient

The absolute or dynamic viscosity of a lubricant is determined by measuring the time of flow of the oil through a capillary of definite dimensions at uniform temperature.

Viscosity generally decreases with increase in temperature. The maintenance of viscosity over the range of temperature is called the viscosity Index (V.I). A relatively small change/no change in viscosity with temperature is indicated by high viscosity index whereas low viscosity index shows relatively large change in viscosity with temperature. There is a direct correlation between molecular structure of lubricating oil with its viscosity and viscosity index. A high viscosity index is exhibited by those lubricating oils which have linear or rod like shape molecules with high molecular weight. This is due to the greater intermolecular forces of attraction. Viscosity of lubricating oil is inversely proportional to the temperature i.e. with increase of temperature, viscosity decreases. This is due to the decrease in intermolecular attraction. At higher temperature, oil must have sufficient viscosity to carry loads. Hence heavier oils are used at higher temperature. Similarly, light oils are used at low ambient temperature. Lubricating oils are subjected to extreme pressure at the interphase between gears and rolling element. At such higher pressure, viscosity of lubricating oil increases considerably.Viscosity helps in selecting good lubricating oil.

Light oils	**Heavy Oils**
Having low density	High density
Easy flow ability	Low flow ability
Used for; High speed, low pressure & Low temperature	Used for; Low speed, high pressure & high temperature

The instruments used for measuring the viscosity are known as viscometers. Different types of viscometers are

• Saybolt Viscometer • Angler's Viscometer • Ostwald Viscometer
• Kinematic Viscometer • Redwood Viscometer

Redwood Viscometer

It is of two types

a) Redwood viscometer No.1- Universal b) Redwood viscometer No.2- Admiralty

Both the above viscometers are identical in principle, shape and mode of testing. The essential differences between the two are

	Redwood viscometer No.1- Universal	Redwood viscometer No.2- Abmiralty
Dimensions of orifice	Length-10mm, Dia-1,62mm	Length-50mm, Dia-3.8mm
Kohlrausch flask	Smaller mouth	Wider mouth
Useful for	Low viscous oil having flow time between 30s-2000s e.g. Kerosine oil and mustard oil	Higher viscous oils having flow time greater than 2000s e.g. Fuel oil, mobile oil

The rate of discharge of oil through RW_2 is nearly 10 times the discharge through RW_1. So, The RW_2 receiving flask has a wider mouth.

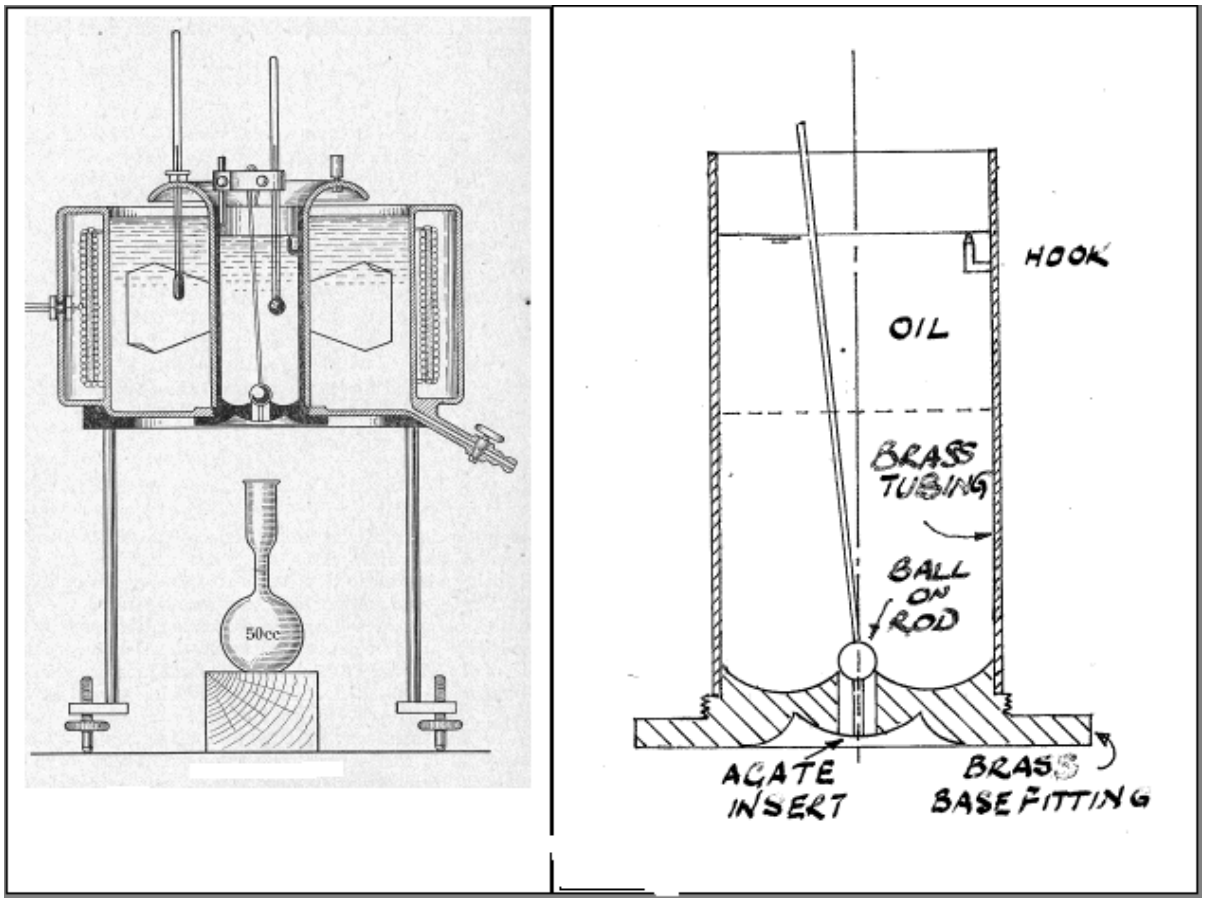
Redwood viscometer is divided in to three parts:

1. **Oil Cup (**Material- Silver plated brass; Height-90mm; Diamtere-46.5mm)

It holds the test sample of lubricating oil. The bottom of the cup is fitted with polished-agate discharge tube containing an orifice of specified dimension

2. Water Bath: Oil cup is surrounded by water bath for adjusting the temperature

3. Kohlrausch Flask: It receives the oil from polished-agate discharge tube



Procedure:

Select the appropriate viscometer, either Redwood viscometer No.1 or 2 depending upon the nature of lubricating oil. Clean the viscometer cup properly with the help of suitable solvent e.g. CCl_4, ether, petroleum spirit or benzene and dry it to remove any traces of solvent. Level the viscometer with the help of leveling screws. Fill the outer bath with water. Place the ball valve on the jet to close it and pour the test oil into the cup up to the tip of indicator (pointer). Place a clean dry Kohlrausch flask immediately below and directly in line with discharging jet. Insert a clean thermometer and a stirrer in the cup and cover it with a lid. Adjust the temperature of water bath until the oil attains the desired temperature. Lift the ball valve with one hand and start the stop watch with the other hand. Allow the oil to flow till the flask is filled upto 50 mL mark. Stop the stop watch when lower meniscus of the oil reaches the 50 ml mark on the neck of receiving flask and note down the time of flow in seconds. Repeat the experiment 3-4 times and record the readings. Report the mean value in Redwood seconds also mentioning the viscometer used and the test temperature.

Observations:

Table: For time of Flow

S.No.	Temperature (°C)	Time of flow (RW seconds)

Mean =

Result:

Viscosity of given lubricant oil is ……RW_1 or RW_2 sec.

EXPERIMENT: To d**etermine the strength of HCl solution by titrating it with NaOH solution conductometrically.**

Apparatus Used:
Conductivity meter, Conductivity cell.

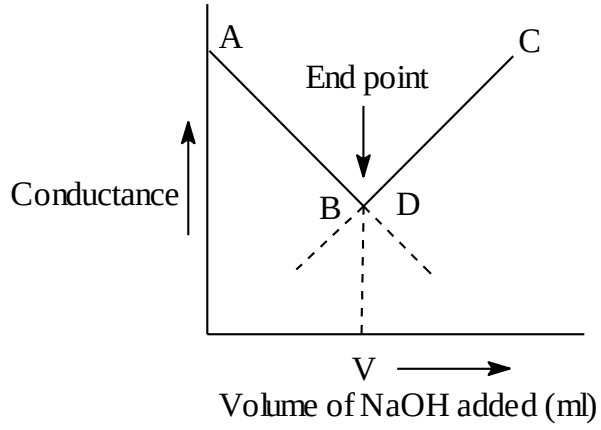
Chemicals Required:
N/10 Sodium hydroxide solution (NaOH), N/100 Hydrochloric acid solution, Distilled water.

Theory:
End point of a volumetric analysis can also be found by conductometric titration which involves measurement of conductance of a solution during titration.

Principle

Electrolytic conductance varies during the course of titration as its depend upon the number of ions in solution and their mobilities.

The end point is found from a plot of conductance values against volume of titrant added which gives two lines intersecting each other. The point of intersection gives the end point of titration.



Titration of HCl vs NaOH (strong acid vs strong base) is studied by titrating a known volume of acid against standard alkali and measuring conductance of solution at different times. Initally the conductance is high as HCl is a strong electrolyte and is highly ionized. On adding NaOH from burette, the conductance decreases. It is because fast moving H^+ ions of HCl are neutralized and are replaced by slow moving Na^+ ions.

$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$

After complete neutralization, added NaOH increases the conductance of solution due to addition of highly mobile hydroxyl ions so the conductivity is minimum at equivalence point. On plotting conductance vs volume of NaOH added, a V – shaped graph is obtained. The point of intersectionof two lines gives end point. From volume of NaOH used at end point, the strength of HCl solution can be determined.

Procedure:

In conductometric titrations, conductance of solution is measured with the help of a conductivity meter in following two steps:

Step 1. Calibration of conductivity meter

1. Switch on the instrument and wait for 2-3 minutes.

2. Connect the conductivity cell to the terminals provided at the back of instrument.

3. Take distilled water (D.W.) in a 100 mL beaker and dip the conductivity cell in it.

4. Set the temperature control knob at 25 °C.

5. Put the cell constant knob to the value of cell constant given on the cell.

6. Select the proper conductance range by putting the multiplier switch in proper range.

   1. Adjust calibration control knob to get the desired value of conductivity of D.W.
   2. The instrument is now calibrated and the calibration control knob should not be disturbed till experiment is complete.

Step 2. Titration of HCl solution vs N/10 NaOH solution

1. Pipette out 50 mL of given HCl solution in a 100 mL beaker.
2. Take out the cell from distilled water and dip in the HCl solution.
3. Push the cal/ meas knob to meas position if required.
4. Note down the conductance value of solution.
5. Add 1 mL of N/10 NaOH solution from burette. Stir thoroughly and note down the conductance of solution when it becomes stable.
6. Add NaOH solution in 1 mL lots and note the corresponding conductance values till the conductance value becomes constant.
7. Plot a graph between conductance (along Y-axis) and volume of added NaOH solution (along X-axis).
8. Find out the volume of NaOH solution used at end point from point of intersection of two lines in the graph.

Observations:

Volume of HCl solution taken = 50 mL

Normality of NaOH solution = 1/10 N

Table: For titration of HCl solution vs NaOH solution

S.No.	Volume of NaOH added (mL)	Observed conductance (mho)
1.	0.0	
2.	1.0	
3.	2.0	
4.	3.0	
5.	4.0	
6.	5.0	
7.	6.0	
8.	7.0	
9.	8.0	
10.	9.0	
11.	10.0	
12.	11.0	
13.	12.0	
14.	13.0	
15.	14.0	

General Calculations:

Say volume of NaOH used at end point (from graph) = V mL

Applying Normality equation

$N_1 V_1 = N_2 V_2$

(HCl) (NaOH)

$N1 \times 50 = 1/10 \times V$

$N_1 = V / 500$ N

Strength of HCl solution = Normality × Equivalent weight of HCl

= V / 500 × 36.5

= X gm/lt

Result:

Strength of given HCl solution conductometrically = X gm/lt

AIM: To determine the total iron(Fe^{2+} and Fe^{3+}) in an iron ore by self indicator method. You are provided N/20 $KMnO_4$ solution.

APPARATUS/CHEMICALS REQUIRED: Burette, Pipette, Titration flask, 100 mL Volumetric flask, Test tube, Filter paper, Zinc dust, Ammonium thiocyanate or potassium sulphocyanide solution and dil. H_2SO_4.

INDICATOR: $KMnO_4$ (self indicator)

END POINT: Appearance of permanent pink colour

THEORY: The iron ore solution contains both Fe^{2+} and Fe^{3+} ions. $KMnO_4$ reacts only with Fe^{2+} and not with Fe^{3+} because Fe^{3+} cannot be further oxidized. For the determination of Fe^{2+} a known volume of iron ore solution is directly titrated against standard $KMnO_4$ in acidic medium (dil. H_2SO_4).

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The amount of Fe^{2+} can be calculated from the volume of $KMnO_4$ consumed. To determine the total iron, all the Fe^{3+} ions in an iron ore solution is reduced to Fe^{2+} by adding Zn dust and H_2SO_4. Zinc reacts with H_2SO_4 to produce nascent hydrogen.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$H^+ + e^- \longrightarrow H\ ] \times 2$$

$$Zn + 2H^+ \longrightarrow Zn^{+2} + 2H$$

The nascent hydrogen so produced reduces Fe^{3+} to Fe^{2+}

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
$$H \longrightarrow H^+ + e^-$$

$$Fe^{3+} + H \longrightarrow Fe^{2+} + H^+$$

To ensure the complete reduction of Fe^{3+} into Fe^{2+}, the solution is tested with KSCN or NH_4SCN as an external indicator which produces red blood colouration with Fe^{3+} ion. If blood red colour comes, reduction is not complete and more zinc dust is added.

$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$
(Ferric thiocyanate)
(Blood red colour)

After the complete reduction excess zinc is removed by filtration or by boiling until the whole of zinc dissolves. The solution is then diluted to a definite volume with distilled water. A known volume of this solution is then titrated with standard $KMnO_4$ in acidic medium till the appearance of light pink colour as end point. The total iron can be calculated from the volume of $KMnO_4$ consumed. The amount of Fe^{3+} is determined by subtracting the amount of Fe^{2+} from total iron.

Amount of Fe^{3+} = Amount of total iron – Amount of Fe^{2+}

PROCEDURE:

Step 1. Determination of Fe^{2+}:

Pipette out 10 mL of iron ore solution in a titrating flask. Add to it 1/3rd test tube of dilute H_2SO_4 and titrate against *N/20* $KMnO_4$ solution till the appearance of pink colour as end point. Repeat the experiment to get concordant reading.

Step 2. Determination of total iron

(a) Reduction of Fe^{3+}: Pipette out 20 mL of iron ore solution in a titration flask. Add pinch of zinc dust and two test tube of dil. H_2SO_4 to it. Warm the mixture slightly and allow the reaction to continue with occasional shaking. When the reaction ceases, take a drop of reaction mixture with the help of glass rod and touch it with the drop of NH_4SCN drop taken on a glazed tile. Appearance of blood red colour indicates the incomplete reduction. In such case add one more pinch of zinc dust to the reaction mixture and test it again as above to see complete reduction. Now boil the mixture, cool and filter in a 100 mL measuring flask. Make up the volume of the flask up to the mark by adding distilled water. Stopper the flask and make the solution homogeneous by shaking the flask up and down.

(b) Titration of reduced solution: Pipette out 20 mL of the filtrate in a titration flask. Add 1/3rd test tube of dilute H_2SO_4 to it and titrate against *N/20* $KMnO_4$ solution till the appearance of pink colour as end point. Repeat the experiment to get concordant reading.

OBSERVATIONS:

Table 1. Titration of iron ore solution Vs *N/20* $KMnO_4$ solution

Sr. No	Initial reading	Final reading	Volume of N/20 20 $KMnO_4$ used (mL)
1. 2. 3.			

Concordant reading = V_1 (say)

TABLE 2. Titration of reduced solution Vs *N/20* $KMnO_4$ solution

Sr. No	Initial reading	Final reading	Volume of N/2020 $KMnO_4$ used (mL)
1. 2. 3.			

Concordant reading = V_2 (say)

GENERAL CALCULATIONS:

Step 1. Determination of Fe^{2+}

Volume of solution taken each time = 10 mL

Volume of $KMnO_4$ used = V_1 mL

Applying Normality Equation:

$$\underset{(Fe^{2+})}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

$$N_1 \times 10 = 1/20 \times V_1$$

$$N_1 = \frac{V_1}{200}$$

$$\text{Strength} = N_1 \times \text{Eg. wt. of iron}$$

$$= \frac{V_1}{200} \times 56 = \text{A g/L}$$

Step 2. Determination of Total iron

100 mL filtrate ≡ 20 mL original iron ore solution

20 mL filtrate ≡ $\frac{20}{100} \times 20$ = 4 mL original iron ore solution

Applying Normality Equation:

$$\underset{(Fe^{2+}\& Fe^{3+})}{N_1V_1} = \underset{(KMnO_4)}{N_2V_2}$$

$$N_1 \times 4 = 1/20 \times V_2$$

$$N_1 = \frac{1}{80} \times V_2$$

$$\text{Strength} = N_1 \times 56 = \text{B g/L}$$

RESULT: Total Iron = B g/L

Fe^{2+} = A g/L

Fe^{3+} = (B–A) g/L

AIM: Determination of concentration of $KMnO_4$ solution spectrophotometrically.

APPARATUS/CHEMICALS REQUIRED: Spectrophotometer**,** Standard $KMnO_4$ solution and Distilled water.

THEORY: The absorption of light in the visible and near ultraviolet regions by a solution is governed by a photophysical law, known as the **Beer-Lamberts law**.

When a beam of monochromatic light of passes through a solution, it is absorbed by the solution. As a result, the intensity of emerged light is considerably reduced. If I_0, I_t and I_a are the intensity of the incident, transmitted and absorbed light respectively, then

$$I_a = I_0 - I_t$$

The rate of decrease in the intensity of a beam of monochromatic radiation with the thickness of solution is directly proportional to the intensity of incident radiation as well as concentration of solution. Mathematically, it can be expressed as

$$dI/dx = -\alpha c I$$

Where dI is the change in the intensity produced by the absorption of radiation on passing through a thickness dx of the solution of concentration c and α is the proportionality constant. The minus sign shows the reduction in the intensity of light.

Integrating the above equation between the limits $I = I_0$ at x = 0 and $I = I$ at x = b, we get,

$$\ln (I/I_0) = 2.303 \log (I/I_0) = -\alpha bc$$

According to above equation **Beer-Lambert law** can be stated as "when a monochromatic light is passed through a sample medium, the intensity of incident light decreases exponentially with increase in the thickness x and the concentration c of the absorbing medium".

Putting $\alpha/2.303 = \varepsilon$ and $A = \log (I/I_0)$, we get

$$A = \log (I/I_0) = \varepsilon bc$$

Where A is the **absorbance** or optical density and ε is called the absorption coefficient or extinction coefficient of the absorbing medium.

If a solution obeys Beer-Lambert law, then the plot of A Vs c is a straight line passing through the origin. This is known as calibration curve .The calibration curve is plotted by measuring the absorbance of standard solution of different concentrations. From the calibration curve, concentration of unknown solutions can be obtained.

Spectrophotometer consists of light source (LS), monochromator (M), detector(D), amplifier (A) and recorder (R).

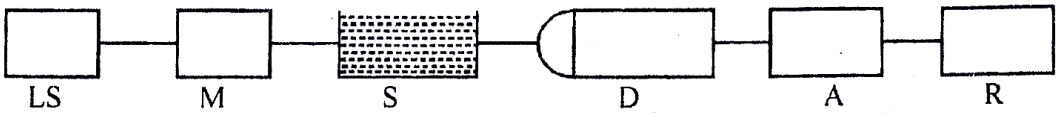


Fig. 10.1. Block Diagram of spectrophotometer

Limitations:

1. The law is not obeyed if the radiation is not monochromatic
2. The law is obeyed only for dilute solutions. At high solute concentrations relationship between A and c is no longer linear.

PROCEDURE:

Step 1. Instruction for the use of Instrument

Part A

(a) Connect the instrument to power supply. Switch on the instrument and ensure that red light indicator glows.

(b) Put instrument on the tungsten filament lamp by rotating the knob marked with 'T' and 'D' so that the visible light passes through the shutter.

(c) Adjust the dark current to zero with the shutter of light closed.

(d) Adjust the wavelength knob to the required wavelength region on the scale. Choose the position of wavelength between 400-960 nm.

(e) Adjust the "zero set" knob so that monitor reads zero on transmittance (T) scale and 100 on optical density (O.D) scale.

Part B

(a) Open the lid of the cell compartment and insert a cuvette containing blank solution (distilled water). Close the lid properly.

(b) Adjust the control knob so that monitor reads 100 on 'T' scale or zero on 'D' scale.

(c) Open the lid and remove the cuvette. Close the lid properly again.

(d) Check zero on the monitor, adjust zero if disturbed.

(e) Repeat again for zero and 100% transmittance.

Step 2. Determination of λ_{max}

(a) Place the cuvette containing standard solution in the cell compartment and note the reading.

(b) Change the wavelength by about 20 nm every time and note down the corresponding optical densities. Plot a graph between wavelength (along X-axis) and O.D.(along Y-axis). Determine the value of λ_{max} by extrapolation of curve towards X-axis.

Step 3. Determination of concentration of sample solution

(a) Fix the wavelength at λ_{max} position.

(b) Prepare 20 mL solution of $KMnO_4$ with concentration 0.2%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3.0% etc.

(c) Note down the optical density of each solution prepared above.

(d) Plot the absorbance against concentration of solution to get a straight line.

(e) Now take a solution of unknown concentration of $KMnO_4$ and note down its optical density. Find out the concentration of unknown solution from the graph corresponding to absorbance of this solution.

OBSERVATIONS:

Table 1. Determination of λ_{max}

S.No.	Wavelength (nm)	Absorbance
1.	–	–
2.	–	–
3.	–	–
4.	–	–

5.	–	–
6.	–	–
7.	–	–
8.	–	–

Table 2. Verification of Beer's law

S.No.	Concentration of $KMnO_4$ solution	Absorbance
1.	0.2	–
2.	0.5	–
3.	1.0	–
4.	1.5	–
5.	2.0	–
6.	2.5	–
7.	3.0	–
8.	Unknown solutions	–

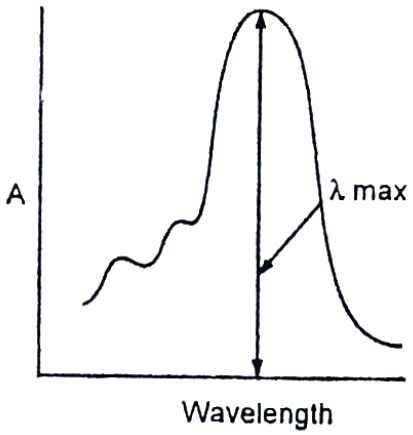


Fig. 10.2. Plot between wavelength and absorbance

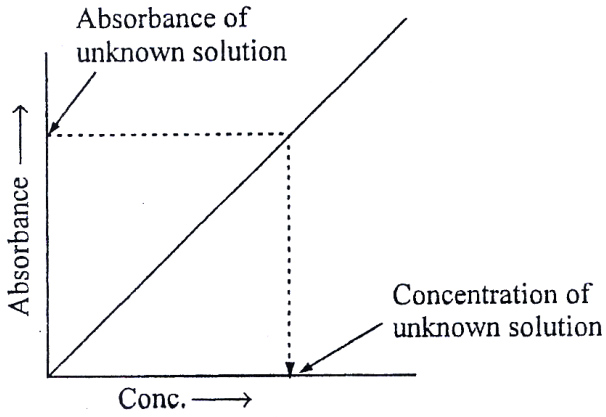


Fig. 10.3. Plot between absorbance and concentration

RESULT: The concentration of given $KMnO_4$ solution spectrophotometrically is ….ppm